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TEKNIIKAN JA LIIKENTEEN ALA

MONITORING ANALYSIS OF PULP AND PAPER INDUSTRIES PILOT SCALE ANAEROBIC WASTE WATER TREATMENT

The acidic wastewater effect on water alkalinity in UASB –type bioreactors

TEKIJÄ: Zhengjie Qi

SAVONIA-AMMATTIKORKEAKOULU

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Työn nimi UASB-tyyppisen anaerobisen jätevesiprosessin seuranta alkaliniteetin suhteen paperi- ja selluteollisuuden jätevesien pilotmittakaavaisessa koelaitteistossa käytettäessä erilaisia syötteitä prosessiin	
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Tässä opinnäytetyössä tutkitaan happaman jäteveden syöttämisen vaikutusta UASB-tyyppisen anaerobisen biokaasuprosessin toimintaan seuraamalla alkaliteetin käyttäytymistä eri vaiheissa prosessia. Happamana jätevetenä käytetään paperi- ja selluteollisuuden kuorimon jätevesijaetta. Työn tavoitteena on tutkia, kuinka happaman jäteveden osuuden lisääminen bioprosessissa vaikuttaa alkaliniteettiin, jolla tietedetään olevan vaikutuksia esimerkiksi metaania muodostavien bakteereiden toimintaan.

Tutkimuksessa bioprosessia seurataan ottamalla näytteitä tulevasta jätevedestä, bioreaktoreiden jätevedestä ja prosessista poistettavasta jätevedestä. Prosessiin syötettävä jätevesi on peräisin suomalaisena paperi- ja selluteollisuuden tuotantolaitoksen jätevesiprosessista. Tutkimuksessa käytetään syötteenä kahdenlaista jätevesivirtaa. Happamampi vesi on kuorimosta tulevaa vettä ja toisena syötteenä on tehtaan aerobisen jätevesiprosessin sisäisestä kierrosta otettu jätevesi

Syötteessä on huomattava määrä orgaanista ainesta, joka muuttuu anaerobiprosessin aikana metaaniksi ja hiilidioksidiksi. Metaanin saanto on suotavaa, koska siitä voidaan tuottaa energiaa.

Avainsanat
Alkaliteetti, biokaasu, metaania muodostavat bakteerit, UASB-reaktori, paperi- ja selluteollisuus, jätevesi

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THESIS
Abstract

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Supervisor(s)
Principal Lecturer Pasi Pajula, Project Engineer Maarit Janhunen

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Savonia University of Applied Sciences Ltd

Abstract

In this thesis is intended to study how the acidic waste water inflow increase into a UASB-type bioreactor influences the water alkalinity concentration in the biological process. The acidic influent increase is coming by adding pulp and paper industries debarking plant’s wastewater into the process. The goal of the thesis is to find out wheather this more acidic influent is affecting the activity of biogas process and especially the methanogenic bacteria in a point of view of alkalinity analysis.

During experiment water samples for alkalinity analysis are being taken from influent, reactor 1, reactor 2 and effluent leaving the process. Influent is the wastewater from Finnish forest industry. Two different kind of wastewater streams are being used in different kind of ratios. The more acidic wastewater stream is coming from debarking plant wastewater while the rest of the influent is from the aerobic wastewater treatment plant circulated wastewater steam.

In the influent there is a considerable amount of organic material and during the anaerobic treatment the microbes are eating the organic material and producing biogas, which can be used for energy production.

Keywords
Alkalinity, biogas, methanogenic bacteria, UASB-reactor, pulp and paper industry, wastewater

CONTENTS

1 INTRODUCTION

Nowadays, more and more industrial plants are using fixed membrane anaerobic digestors to treat soluble organic compounds in their wastewater. In this study anaerobic digestors are being researched in treating sludge and soluble waste from Finnish pulp and paper industries waste streams. At the same time maximizing biogas production is optimized by studying alkalinity's role in the process.

Finnish pulp and paper Industry Wastewater usually has high concentrations of sulfate, ammonium and carbon compounds in their effluents, which can contaminate the receiving waters, cause eutrophication and endanger life if these emissions are not treated in a proper way before discharging them into receiving waters. Also by utilizing anaerobic digestion we can utilize the energy of organic material instead of wasting it in traditional aeration ponds.

Chemical oxygen demand (COD), ammonium and sulfate are often discharged together in industrial wastewater. Anaerobic treatment of some of the wastewater streams from pulp and paper factory provides a promising new approach to treat the wastewater not losing the energy in organic material. All wastewater streams are not suitable for the purpose, but there seems to be suitable water streams for the purpose to make the anaerobic treatment also economically feasible. Alkalinity of the wastewater is one of the key factors affecting microbe liveness in an anaerobic digester.

1.1 Background

Anaerobic digestors with suspended bacterial growth are commonly used in urban wastewater treatment plants to degrade (digest) sludge. The target of the anaerobic digestor is to destroy most of the volatile solids in the sludge and minimize the corrosiveness of the sludge.

The main products of the anaerobic digestion tank are biogas and harmless digestion sludge solids. Biogas is mainly composed of methane (CH_4) and carbon dioxide (CO_2). In anaerobic sludge digestion a series of microbiological processes change organic compounds into methane, carbon dioxide and new bacteria.

1.2 Objective

In this paper, through the "alkalinity analysis" experiment, which is being done by recording the volume of hydrochloric acid consumed, and calculating the alkalinity change by a specific formula, we are evaluating how debarking plant's waste water is influencing the activity of biogas process and the methanogenic bacteria from the point of the acidic waste water effect on water alkalinity concentration.

1.3 Methods: Alkalinity Analysis of Activated, Residual and Bio-gasified Sludge

Alkalinity in bio-gasified, activated and residual sludge can be analysed potentiometrically. Alkalinity means the process's capacity to resist changes in pH caused by hydroxides, carbonates and hydrogen carbonates as well as by silicates, phosphates, borates, arsenates and aluminates.

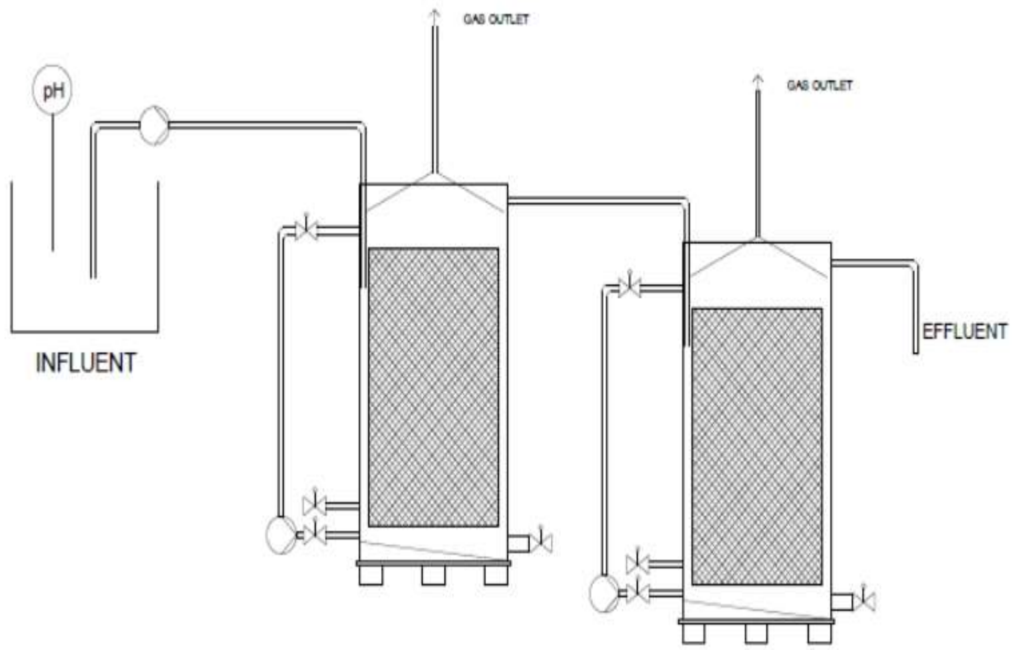

Figure 1. Laboratory equipment process diagram

In this study a two stage anaerobic process is being used. The process can be seen in Figure 1. Most of the organic carbon removal takes place in reactor 1. The gray area is fixed bed column reactor which contains plastic fillers. Methanogenic bacteria accumulate on the surface of the plastic filling plates, where the bacteria starts to multiply themselves.

Process parameters are including retention time of 24 hours in the whole process, temperature of + 38 °C, organic loading of 5 000 mg COD/Rm^3/d and pH value 7. Granulation on plastic fillers can be strengthened by calcium and iron.

In the two stage process there is internal circulation inside the reactors, which serves as mixing the process. During the process the buffer capacity of the water will be rising as methanogenic bacteria activity rises the levels of CO_2, HCO_3 and NH_3. All of the organic matter is not removed in the process. Part of the organic material is settling to the bottom of the reactor and the rest is transforming into methane and carbon dioxide or going through the process. About 80 % organic carbon will be removed on reactor 1, and reactor 2 verify the effectiveness of reactor 1. The gas is collected in both of the reactors in a separate gas collection bags and analyzed with the volume and the content which includes CH_4, CO_2, O_2 and H_2S.

2 LITERATURE

2.1 Bioreactor

The bioreactor used in this experiment is a wet digester equipped with a fixed bed reactor (UASB-technology). The Upflow Anaerobic Sludge Blanket (UASB) reactors have been most widely used in these kind of applications. The alkalinity level is usually between 3 500 – 5 000 mg $CaCO_3$/l in wet digestors. But in wet digestors which are equipped with UASB -technology, alkalinity should been between 250-950 mg $CaCO_3$/l.

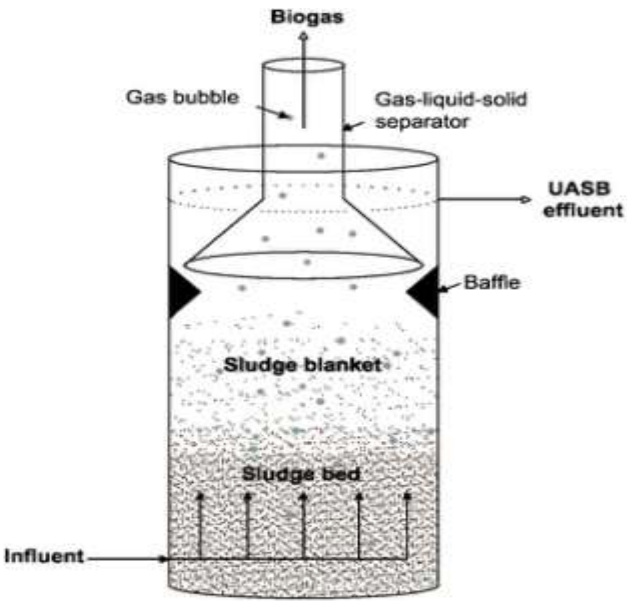

Figure 2. Schematic of a UASB reactor (Lettinga and Hulshoff Pol, 1991).

The schematic diagram of a UASB reactor is shown in Figure 2. The reactor consists of two parts: a cylindrical or rectangular column and a gas-liquid-solid (GLS) separator (Lettinga and Hulshoff Pol, 1991). UASB reactors are initially inoculated with inoculants such as digestion, anaerobic, granulated, flocculent and activated sludge. The sludge enters from the bottom of the reactor..

Under suitable conditions, the light and dispersed particles will be removed while the heavier components will be retained to minimize the growth of finely divided sludge while forming an inert organic, inorganic and small particles of aggregates or flocs (Hulshoff Pol et al., 2004). After a certain period of time (usually 2-8 months), depending on the operating conditions and characteristics of the wastewater and seed sludge, a very dense sludge bed has been developed that may have a high sedimentation property.

Above the dense sludge bed, there is a sludge blanket zone with a much diffused growth and lower particle setting velocities (Aiyuk et al., 2006). The biological reactions take place throughout the highly active sludge bed and blanket zone. As the flow passes upward, the soluble organic compounds in the influent are converted to biogas consisting of mainly methane and carbon dioxide. The produced biogas and the sludge buoyed by the entrapped gas bubbles are then separated from the effluent by the immersed GLS separator, in which the baffles prevent as efficiently as possible the wash-out of the viable bacterial matter or floating granular sludge by sliding the settled solids back to the reaction zone (Lettinga and Hulshoff Pol, 1991; Hickey et al., 1991).

2.2 Biogas

The only economically significant gas produced in an anaerobic digester is methane. Methane can be used as a fuel source. It is a natural flammable gas. Methane is odorless and burns cleanly (Equation 2.1). Pure methane has a heating value of 37256.772 J/l. When methane is mixed with the carbon dioxide produced in the anaerobic digester, its calorific value is significantly reduced.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (2.1)

Gas production, particularly methane, increases as the organic load to the digester increases, until methane-forming bacteria are no longer able to degrade volatile acids. The volume, rate and composition of the generated biogas indicates the cooker performance. Acceptable or normal ranges for biogas production are 6.72-16.80 m^3/kg volatile suspended solids (VSS) converted at 25^oC or 0.4 to 0.6 l/g chemical oxygen demand (COD). The disposability of waste or substrates by anaerobic digesters is usually determined by monitoring biogas production. The rate and volume of methane produced during the anaerobic digestion of the waste can be used to determine its relative conversion. (Michael H. G)

2.3 Microbiology and parameters affecting microbiological processes in anaerobic digestion

The efficiency of AD is influenced by some key parameters, thus providing the appropriate conditions for anaerobic microorganisms to be critical. (Teodorita Al S, Dominik R, Heinz P, Michael K, Tobias F, Silke V, Rainer J.)

pH-values and optimum intervals

The pH is a measure of the acidity / alkalinity of the solution of the substrate mixture in the case of AD, expressed in parts per million (ppm). The pH of the AD substrate affects the growth of methane-producing microorganisms and affects the dissociation of some of the compounds that are important for the AD process. The compounds are usually ammonia, sulfide and organic acids. (Teodorita Al S, Dominik R, Heinz P, Michael K, Tobias F, Silke V, Rainer J.)

Experience has shown that methane formation occurs in a relatively narrow pH range of about 5.5 to 8.5, and the optimum interval for most methanogens is 7.0-8.0. Acidic microorganisms usually have a lower optimum pH. (Teodorita Al S, Dominik R, Heinz P, Michael K, Tobias F, Silke V, Rainer J.)

The optimum pH interval for the digestion is 6.5-8.0, and if the pH is reduced to 6.0 or higher or above 8.3, the process is severely inhibited. The solubility of carbon dioxide in water decreases with increasing temperature. Thus, the pH in the thermophilic digestion tank is higher than that of the thermophilic digester because the dissolved carbon dioxide reacts with water to form carbonic acid. (Teodorita Al S, Dominik R, Heinz P, Michael K, Tobias F, Silke V, Rainer J.)

The pH can be increased by the presence of ammonia in the process of protein degradation or the presence of ammonia in the feed stream, while the accumulation of VFA reduces the pH. (Teodorita Al S, Dominik R, Heinz P, Michael K, Tobias F, Silke V, Rainer J.)

The pH in the anaerobic reactor is primarily controlled by the bicarbonate buffer system.

Thus, the pH in the digester depends on the partial pressure of CO2 and the concentration of alkaline and acid components in the liquid phase. If the accumulation of alkali or acid occurs, the buffer capacity to a certain extent, offset these changes in pH. When the buffer capacity exceeds the system, the rapid change in pH completely inhibits the AD process. Therefore, pH is not recommended as a separate process monitoring parameter. (Teodorita Al S, Dominik R, Heinz P, Michael K, Tobias F, Silke V, Rainer J.)

The buffer capacity of the AD substrate can vary. Denmark's experience shows that, the buffering capacity of cow dung varies with the seasons and may be affected by combination of cattle feed. Thus, the pH of the livestock manure is a variable that cannot be trusted as a process imbalance indicator as it changes very little and very slowly. However, it is important to note that pH can be a fast, relatively reliable and cheap way to register the system imbalance in the weaker buffer Systems such as AD for various types of wastewater. (Teodorita Al S, Dominik R, Heinz P, Michael K, Tobias F, Silke V, Rainer J.)

3 DESIGN AND PLAN FOR THE LAB EXPERIMENTS

3.1 Introduction

Influent is waste water from Finnish pulp and paper industry, which is composed of different proportions of recycled plant wastewater and debarking plant wastewater. Empirical results from my project show that organic acids/alcohols found in the debarking plant waste water are:

- Acetic acid (around 250 mg/l)
- Propionic acid (200 mg/l)
- Methanol (around 9 mg/l)
- Ethanol (100 mg/l)
- Butane diol (30 mg/l)

The organic acids/alcohols from plant's recycled wastewater are:

- Formic acid (10 mg/)
- Asetic acid (500 mg/l)
- Butyric acid (130 mg/l)
- Propionic acid (200 mg/l)
- Lactic acid (1 200 mg/l)
- Methanol (2 mg/l)
- Ethanol (50 mg/l)
- Butane diol (40 mg/l)

Effluent is the waste water which has gone through the biogas process through the bio-reactors. Influent consist quite much organic material. In bio-reactors microbe is eating the organic material and produce biogas.

During experimental time, samples are taken from Influent, Reactor 1, Reactor 2 and Effluent. There are four steps in the operational process of AD. First, recycling plant wastewater and debarking plant wastewater are mixed as influent in different ratios. Second, the influent flows into reactor 1. Third, outgoing wastewater flows into reactor 2. Finally, all effluent flows into effluent tank. Meanwhile, biogas is collected from both reactors.

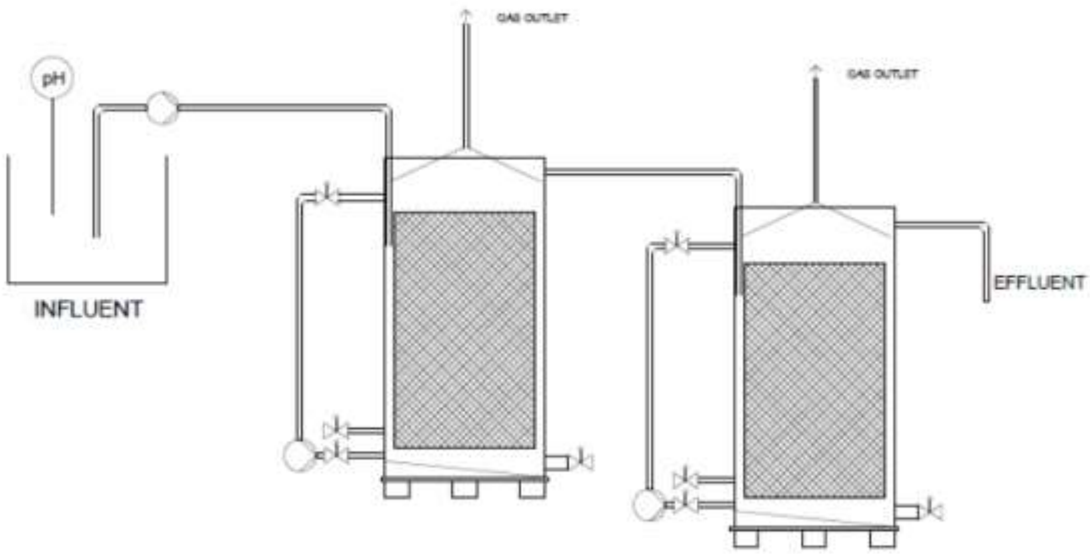

Figure 3. Laboratory equipment process diagram

The UASB-process used in these tests can be seen in Figure 3. The process is a two stage anaerobic process, where reactor 1 removes the most of the organic carbon.

3.2 Reagents and methods used in the tests

In these experiments, reagents are deionized water and hydrochloric acid (0.1 mol/l). The needed apparatus are respectively centrifuge, 50 ml sample tubes, pH meter, 50 ml burette and 50 ml titration flask. In Figure 3.2 there is sample come from reactor 1. The pH meter used in thsts is can be seen in Figure 3.3.

Figure 3.2 Sample from reactor 1 Figure 3.3 pH meter (manufacturer: wtw, model 3210.)

It can be seen in Figure 3.2 that after the sample has been centrifuged, the sludge was separated from sample. The sample became clear. After this it is easy and accurate to detect the alkalinity.

The pH meter used in this experiment is being shown in Figure 3.3. The pH meter is accurate to three decimals.

3.3 Laboratory analysis method for alkalinity analysis of activated, residual and bio-gasified sludge

In experimental laboratory studies, the goal is to record the amount of hydrochloric acid used when titrating the sample to pH = 4.5. The needed reagents are deionised water and hydrochloric acid (0.1 mol/l). The instruments used are centrifuge, 50 ml sample tubes, pH meter, burette(50 ml), titration flask(50 ml).

During sampling time, samples were taken respectively from Reactor 1, Reactor 2, Influent and Effluent. The volume of one sample was about 120 ml. Centrifugal machine was used for separating sludge from the samples. The centrifuge and centrifuging tubes can be seen in Figures 3.4 and 3.5. The centrifuge was run using 13000 rpm with 20 minutes centrifuging time.

Figure 3.4 Centrifuge tubes

Figure 3.5 Centrifuge machine

Centrifuging tubes numbers 1-3 were filled with samples from reactor 1. Numbers 4-6 were filled with samples from reactor 2.

For each sample, two conical flasks were needed with 50 ml of sample without any sludge was taken from the tubes into each conical flask. Each sample was stirred after this with hob and magnet. Hydrochloric acid (0.1 mol/l) was being titrated into the sample until the pH level of 4.5 was being achieved, recording the pH and HCl volume during the experiment.

The samples can be seen in Figures 3.6 and 3.7. The color of samples was significantly different from each other from each phase of process. The color was from buff to red-brown from reactor 1 to effluent.

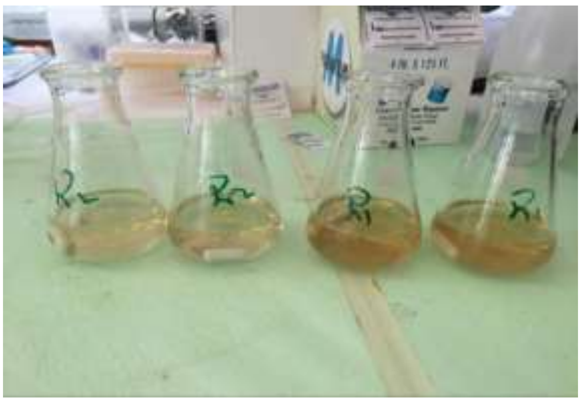

Figure 3.6 Samples of reactor 1 and reactor 2.

Figure 3.7 Samples of Effluent

Equation 3.1 was used for calculating the alkalinity.

$$\text{Alkalinity} = (50000*M*A)/V \qquad (3.1)$$

, where

M is molarity of hydrochloric acid (0,1 mol/l)

A is consumption of titrant, i.e. acid, in millilitres

V is volume of sample in millilitres

The series of experiments took place during weeks 8, 9, 11 and 12 in 2017. Each week the same procedure was carried out on Monday, Wednesday and Friday. The influent for the process during the experiments can be seen from table 3.3.

Table 3.3 Biogas process

Bioreactor process	
week	Amount of debarking plant wastewater
2017	%
6	10
7	10
8	20
9	20
10	30
11	30
12	30

influent is waste water coming from debarking plant (acidic), rest (100 % - amount of influent) is recycled wastewater from wastewater treatment plant

During experimental time, in the first two weeks, the amount of Influent was 10%. On week 8 and 9 the process influent was composed of 20% share of debarking plant's watewater and 80% share of recycled wastewater from wastewater treatment plant. Last three weeks were run by using influent where the share of debarking plant wastewater was 30% and 70% was recycled wastewater.

The debarking plant's wastewater is very acid, the pH is around 4. Through adding different ratios of two different wastewater streams into the UASB-process it is studied how the debarking plant wastewater affects alkalinity concentration.

4 RESULTS

Corresponding the literature, alkalinity should be between 250-950 mg $CaCO_3$/l in UASB-reactor (Siewhui C a,*, Tushar Kanti S a, Ahmet K b, Ha Ming A a.1807). This level should be presented in the influent, but in the reactors alkalinity is rising because the internal circulation raises the levels of CO_2, Ammonia (NH_3) and bicarbonate (HCO_3) in the system . The endpoint of alkalinity titration in the carbonate system depends on the carbon dioxide content at the end of the titration process. It is believed that the alkalinity level between 250 and 950 mg CaCO3 / l favors the formation and stability of the particles in the UASB reactor (Singh RP, Kumar S, Ojha CSP.1999). The carbon dioxide content depends on the original carbonate and bicarbonate/hydrogen carbonate concentration of the sample and titration isn't continued until a certain pH value is reached. It is generally considered that the alkalinity value is equal to the amount salts of carbonic acid.

Table 4.1 Alkalinity results of the whole six weeks (The unit is Alkalinity CaCO3 mg/l)

Week 6	Influent	R1	R2	Effluent	Week 9	Influent	R1	R2	Effluent
Monday	0	0	0	0	Monday	925	1560	1815	1660
Wednesday	0	0	0	0	Wednesday	1010	1420	1705	1640
Friday	690	1575	1500	1255	Friday	0	0	0	0
Average	690	1575	1500	1255	Average	968	1490	1760	1650
Week 7	Influent	R1	R2	Effluent	Week 11	Influent	R1	R2	Effluent
Monday	735	1400	1625	0	Monday	950	1290	1555	1510
Wednesday	795	1580	1675	1415	Wednesday	995	1355	1640	0
Friday	635	1435	1605	1555	Friday	970	1435	1665	1655
Average	722	1472	1635	1485	Average	972	1360	1620	1583
Week 8	Influent	R1	R2	Effluent	Week 12	Influent	R1	R2	Effluent
Monday	605	1325	1580	1310	Monday	900	1485	1675	1555
Wednesday	875	1585	1720	1495	Wednesday	980	1485	1790	1750
Friday	880	1720	1810	1550	Friday	0	1315	1565	1565
Average	787	1543	1703	1452	Average	940	1428	1677	1623

The results of alkalinity during the whole six weeks has been shown in Table 4.1. There was no any results on Monday and Wednesday in week 6. Because the starting date of experiments was on Friday, 10 February in week 6. There was no experiment on Friday in week 9. Because of the lack of effluent, there was no results of effluent on Monday in week 7 and Wednesday in week 11. The same situation of Influent happened on Friday in week 12.

Compared the results, something are easy to be found. Firstly, the whole results of influent is lower than the results of reactor 1, reactor 2 and effluent in the same day. Because in the reactors, alkalinity is raising because of the rising levels of CO_2, ammonia (NH_3) and bicarbonate (HCO_3) of internal circulation. Secondly, the results of reactor 2 are higher than that of reactor 1 when they are compared in the same day only except week 6. It proved that the level of CO2, ammonia (NH3) and bicarbonate (HCO_3) in reactor 2 was higher than in reactor 1. Finally, the results of effluent is a little bit lower than that ofreactor 2.

Influent is the wastewater from Finnish forest industry, which is mixed with recycled wastewater from wastewater treatment plant and debarking plant wastewater. The amount of debarking plant wastewater is always less than recycling plant wastewater, because debarking plant wastewater is very acid, the pH is 4.

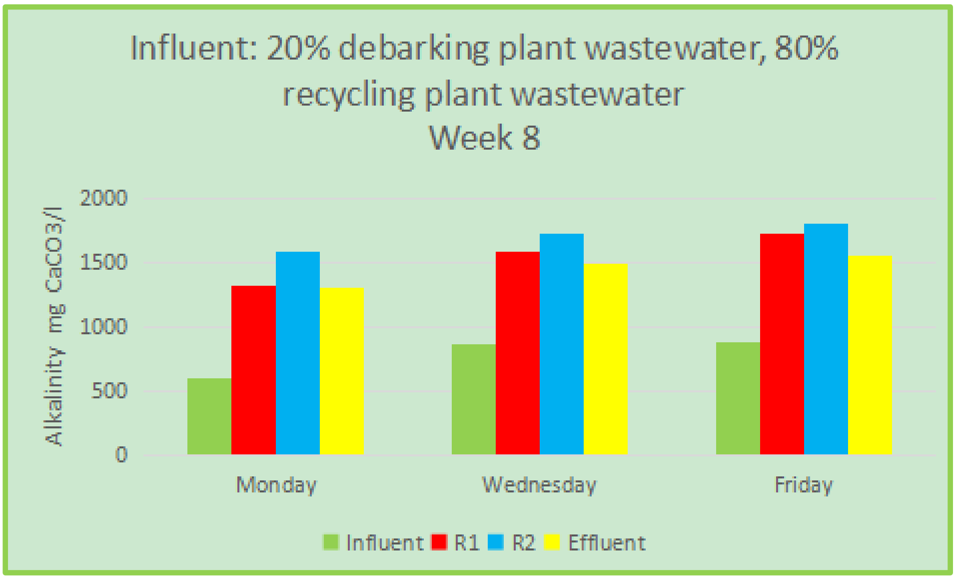

Figure 4.1 Alkalinity results of week 8.

From figure 4.1 above, all the results of influent during week 8 are between 250-950 mg $CaCO_3$/l (Siewhui C a,*, Tushar Kanti S a, Ahmet K b, Ha Ming A a.1807). On Monday, the results is raising from influent to effluent. The phenomenon is the same also on Wednesday and Friday. Alkalinity is raising in reactors which proves that the internal circulation raises the level of carbon dioxide, ammonia (NH_3) and bicarbonate (HCO_3).

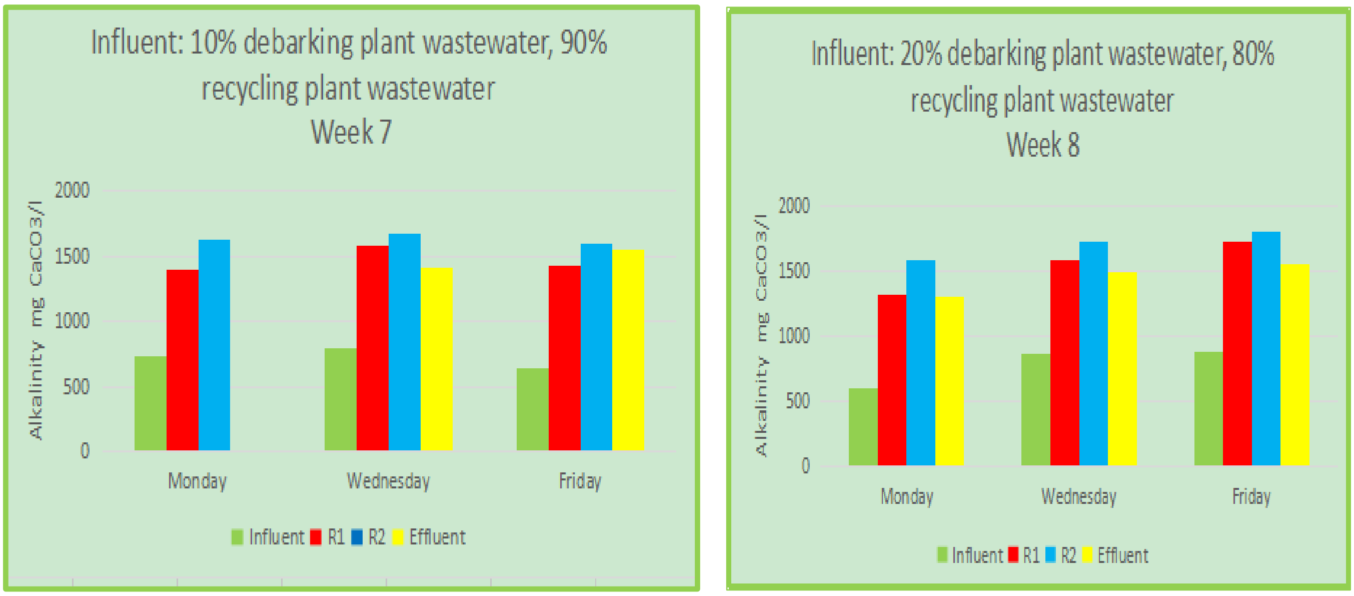

Figure 4.2 Alkalinity results of week 7 and week 8. (There was no Effluent sample on Monday in week 7.)

Alkalinity results of week 7 and week 8 can be seen in Figure 4.2 above. Comparing the results of week 7 with week 8, there is two points to state. On the one hand, the alkalinity is raising during both weeks from Influent to Effluent. On the other hand, whole of the results in week 8 is not such higher than the same type in week 7 as expected.

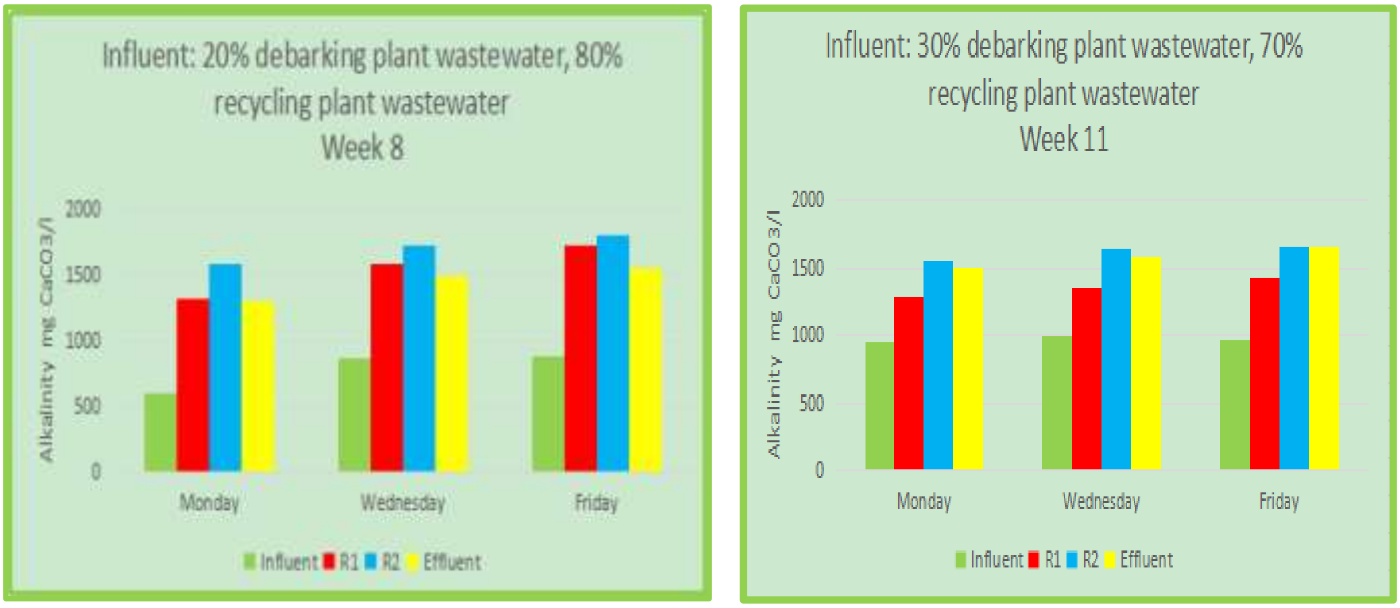

Figure 4.3 Alkalinity results of week 8 and week 11.

The alkalinity results for week 8 and week 11 can be seen in Figure 4.3. When comparing week 8 to week 11, the alkalinity results of Influent in week 11 are little higher when compared to week 8.

5 DISCUSSION

During the test weeks the UASB-process was behaving as expected. During the process, alkalinity is rising, which proves that the activity of methanogenic bacteria is good. Also the levels of CO2, HCO3 and ammonia are rising.

The process is doing well. Methanogenic bacteria activity is high.

From empirical result of the experiment, organic acids/alcohols found in the debarking plant wastewater and recycling plant wastewater are in Table 5.1 :

Table 5.1 Components of debarking plant waste water and recycling plant waste water.

Organic acids/alcohols			
debarking plant waste water		**recycled plant waste water**	
	Amount(mg/l)	**type**	**Amount(mg/l)**
Acetic acid	≈250	Formicacid	10
Propionic acid	200	Asetic acid	500
Methanol	9	Butyric acid	130
Ethanol	100	Propionic acid	200
Butane diol	30	Lactic acid	1200
		Methanol	2
		Ethanol	50
		Butane diol	40

With the increasing percentage of debarking plant wastewater, organic acids/alcohols are also increasing. Most of these are lower fatty acids or can be transferred into lower fatty acids.In the UASB reactor with the addition of lower fatty acids such as acetic acid, there is no need for acidity and acetic acid-producing microorganisms, and only methanogenic bacteria are required to complete the anaerobic degradation process. Thus, in such a reactor, the strong particles consist of methanogenic bacteria (Grotenhuis JTC, Smit M, Plugge CM, Yuansheng X, Van Lammeren AAM, Stams AJM, et al.1991). In the process, The acidified product is further oxidized to acetate, hydrogen and carbon dioxide, in a step called acetylation (Stams AJM.1994) (Schink B. In: Balows A, Tru ¨ per HG, Dworkin M, Harder W, Schleifer KH, editors. 1992). It is produced by the production of hydrogen hydrogen peroxide (OHPAs). In general, the substrate such as butyrate, propionate or ethanol is oxidized to acetate, hydrogen and / or formate; or acetate, hydrogen / formate and carbon dioxide; is a negative reaction. (Schink B. In: Balows A, Tru ¨ per HG, Dworkin M, Harder W, Schleifer KH, editors. 1992) (Li YY, Fang HP, Noike T. 1994)

6 CONCLUSION

The study successfully evaluate how the acidic wastewater (debarking plant wastewater) effect of water alkalinity concentration. Acidic wastewater (debarking plant wastewater) is rich in short chain fatty acids and alcohols. The increasing of debarking plant wastewater can result in increased alkalinity. Optimum alkalinity is essential to maintain the reactor pH and buffer significant fluctuations in the VFA concentrations.

With the increasing content of debarking plant wastewater, organic acids/alcohols are also increasing. Most of these are lower fatty acids or can be transferred into lower fatty acids. In the UASB reactor with the addition of lower fatty acids such as acetic acid, there is no need for acidity and acetic acid-producing microorganisms, and only methanogenic bacteria are required to complete the anaerobic degradation process. Thus, in such a reactor, the particles consist mainly of methanogenic bacteria (Grotenhuis JTC, Smit M, Plugge CM, Yuansheng X, Van Lammeren AAM, Stams AJM, et al.1991). In the process, the products of acidogenesis are further oxidized to acetate, hydrogen, and carbon dioxide, in a step called acetogenesis (Stams AJM.1994) (Schink B. In: Balows A, Tru ¨ per HG, Dworkin M, Harder W, Schleifer KH, editors. 1992). It is produced by the production of hydrogen hydrogen peroxide (OHPAs). In general, the substrate such as butyrate, propionate or ethanol is oxidized to acetate, hydrogen and / or formate; or acetate, hydrogen / formate and carbon dioxide; it is a negative reaction. (Schink B. In: Balows A, Tru ¨ per HG, Dworkin M, Harder W, Schleifer KH, editors. 1992) (Li YY, Fang HP, Noike T. 1994)

With the increasing of debarking plant wastewater, acetic acid, propionic acid, methanol, ethanol and butane diol will increase. These organic compounds react to form substrates such as butyrate, propionate, and further form acetate, hydrogen or formate; or acetate, hydrogen / formate and carbon dioxide (Li J, Hu B, Zheng P, Qaisar M, Mei L. 2008). In view of the low sensitivity of pH groups to pH fluctuations compared to methanogens, which requires a pH close to 6.3-7.8, acid formation is more prevalent than methane production. The methanogens can use these substrates to produce methane.

The pH of acidic wastewater is close to 4. Excessive increase in acid waste water will cause the pH of the influent to decrease. When pH is low, acid formation is more pronounced than methane production, resulting in the accumulation of volatile fatty acids (VFA) in reactors (Van Haandel AC, Lettinga G.1994) (Els ER, Keet K.2007). This situation is exacerbated by the fact that acid bacteria are more active in methanogens at lower pH. These conditions can lead to particle decomposition, because methanogenic bacteria may die.

At the same time, with the increase in acid waste water, alkalinity can provide the buffer capacity of the UASB reactor (Florencio L, Field JA, Lettinga G.1995), thus providing a hedge against the sharp changes in pH. Alkalinity also helps to neutralize the VFA concentration fluctuations that often occur due to changes in organic load (Isik M, Sponza DT.2005). As shown in Figure 4.1, the alkalinity results of influent are 250-950 mg CaCO3 / l. The alkalinity increases in the reactor. Alkalinity is buffering the pH change caused by acidic wastewater. Because the internal circulation is raise levels of CO_2, Ammonia (NH_3) and bicarbonate (HCO_3).

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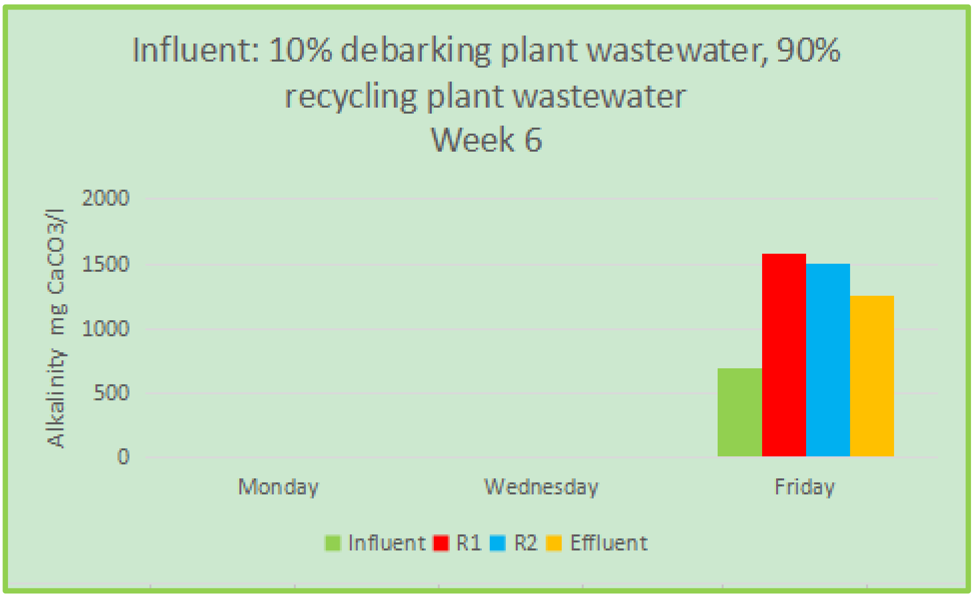
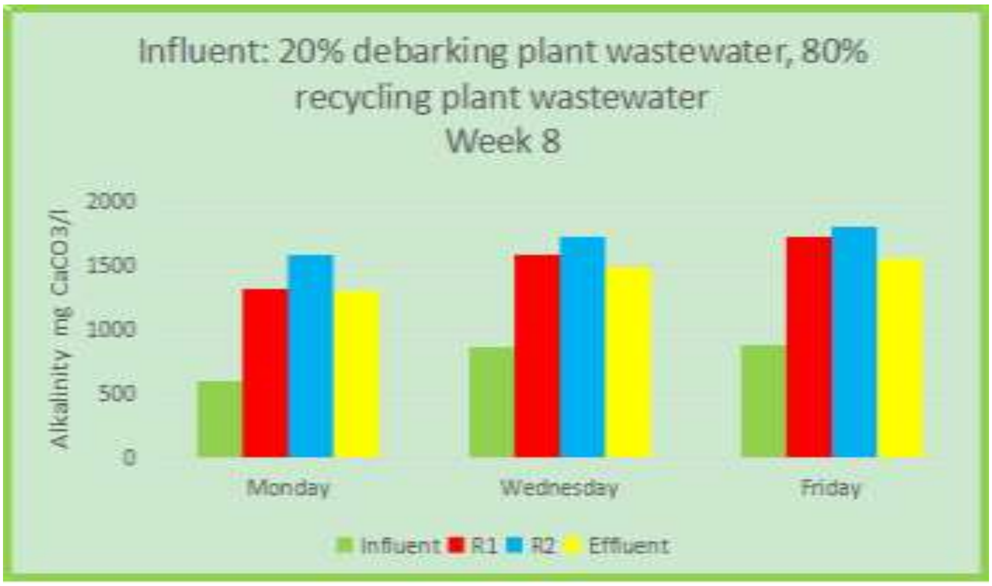
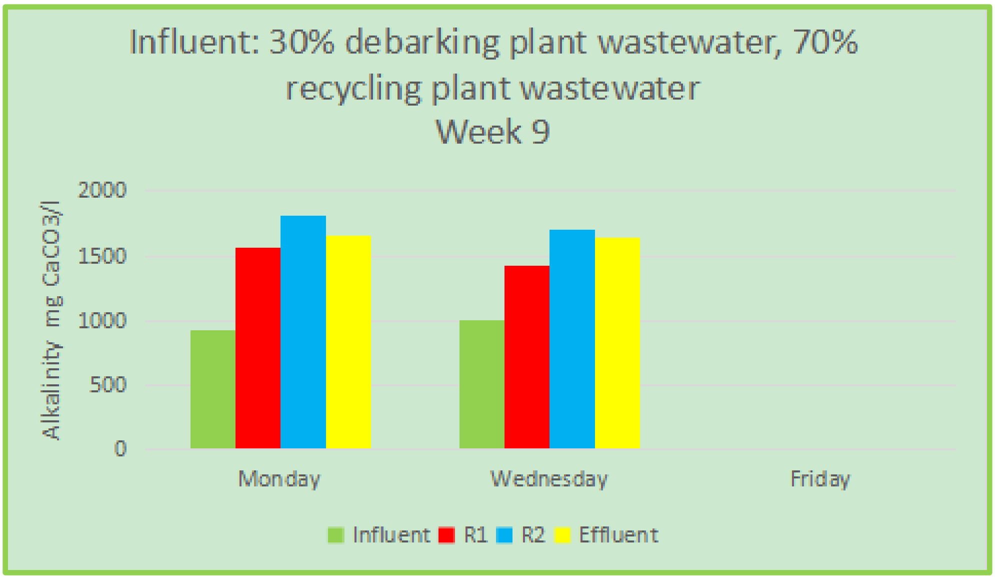
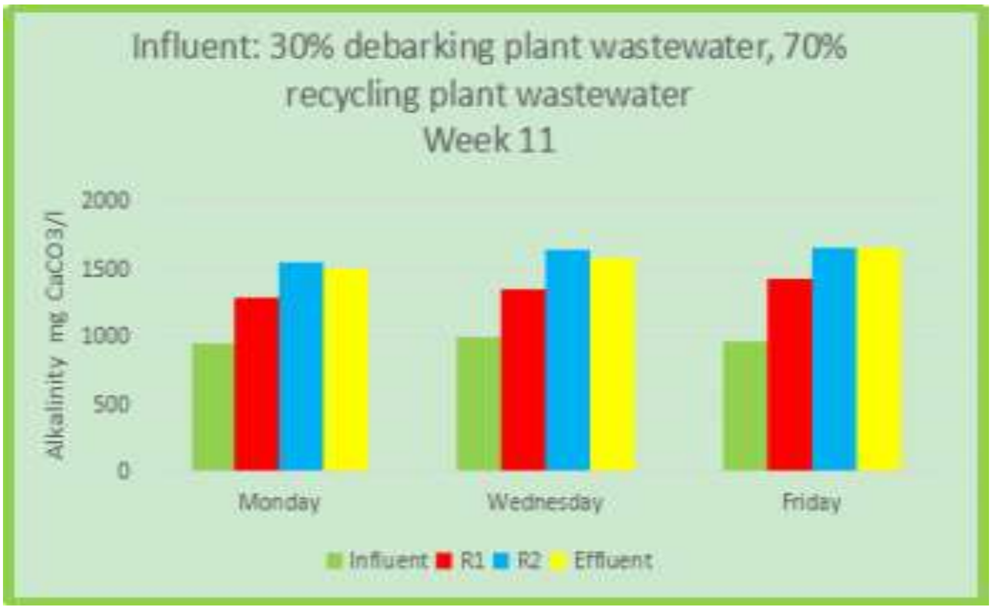
APPENDIX

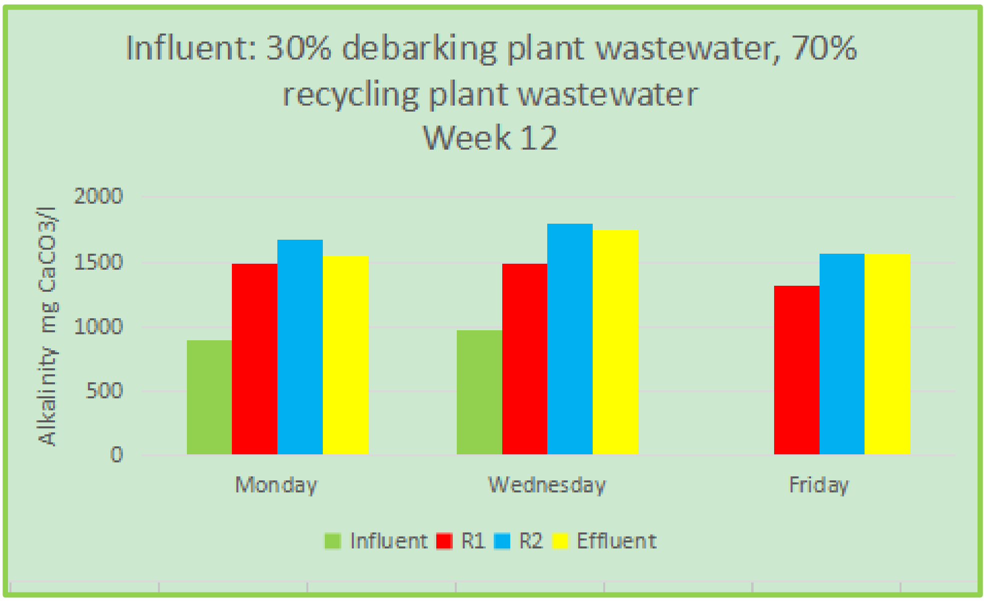
Appendix 1 Different amount of recycling plant wastewater and debarking plant wastewater in Influent






Influent: 30% debarking plant wastewater, 70% recycling plant wastewater
Week 9
Alkalinity mg CaCO3/l
2000
1500
1000
500
0
Monday
Wednesday
Friday
Influent
R1
R2
Effluent


Influent: 30% debarking plant wastewater, 70% recycling plant wastewater
Week 11
Alkalinity mg CaCO3/l
2000
1500
1000
500
0
Monday
Wednesday
Friday
Influent
R1
R2
Effluent


Influent: 30% debarking plant wastewater, 70% recycling plant wastewater
Week 12
Alkalinity mg CaCO3/l
2000
1500
1000
500
0
Monday
Wednesday
Friday
Influent
R1
R2
Effluent